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Effects of Si content in DLC films on their friction and wear properties

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Abstract

Diamondlike carbon (DLC) has been well known as a very hard and very low-friction material. The most critical issue of DLC is to improve its adhesion. To improve the adhesion, some other elements, such as Si, have been included in DLC films. We have studied the effects of Si content on friction and wear properties of DLC films made by our bipolar pulse PBII system. The content of Si was changed by varying the flow rates of tetramethylsilane (TMS) from 0.0 to 3.5 sccm while the flow rate of toluene and the total pressure was kept constant. Friction coefficients (FCs) were measured with a JIS-SUJ2 (AISI 52100) ball of 3-mm diameter. The length of sliding was 2 mm, the speed was 10 mm/s, and the load was 4.9 N for 40-min tests.

Without TMS flow, the friction coefficients (FCs) were the largest, 0.35, and the DLC film came off easily. With the increase of TMS flow up to 1.0 sccm, the FC decreased to 0.14, and there was almost no peeling off. For 2.0 sccm, the FC was 0.18, and there was a lot of debris on the DLC surface. Hardness gradually decreased with the increase of TMS flow up to 1.0 sccm, and it decreased drastically for high flow rates or high Si content. Internal stress (compressive) of the films decreased with the increase of TMS flow. Si content in the film corresponded almost linearly to the TMS flow rate. One to two percent of Si doping is very suitable for improving the adhesion of films and reducing internal stress while maintaining the surface hardness of DLC films.

Keywords: DLC; PBII; Si Doping; Friction and Wear; Internal Stress

1. Introduction

Diamondlike carbon (DLC) films are of interest because they have excellent mechanical properties, including high hardness, low friction coefficient and high wear resistance. There have been many successes in the practical usage of DLC films in low-stress contact, but there are few successes in mechanical industries. The most critical issues (beside the cost) on commercialization of DLC films in mechanical industries are DLC film formation on complicated shaped materials and durability of DLC films or to improve adhesion strength and to reduce internal stress of films.

Regarding the formation of DLC films on the complicated shaped materials, we have invented a new system of plasma-based ion implantation (PBII) technique, which can apply bipolar (plus and minus) pulsed high voltages to target materials, and have demonstrated the formation of DLC films not only on the outer wall of stainless pipes but also on the inner wall [1,2]. Our system is very suitable for depositing DLC coatings on complicated shaped materials, because the target material itself is used as an electrode for plasma formation, and any external plasma sources are not necessary.

To improve the adhesion strength and to reduce the internal stress of DLC films, doped DLC films by other elements prepared by plasma-enhanced chemical vapor deposition (PECVD) have been studied, especially on Ti, W and Si [3]. Recently, many researchers have reported that Si doping can improve adhesion strength and can reduce the internal stress [3–5]. In this paper, we have studied the effects of Si content on friction and wear properties of DLC films made by our bipolar pulse PBII system.

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2. Experimental

An outline of our PBII system using bipolar pulses has been described in our previous papers [1,2]. In this study, we have used a new system, which has a chamber of 600 mm in diameter and 600 mm deep with very large peak current (up to 50 A) pulse power supplies.

Toluene ($C_6H_5CH_3$) was used as a precursor gas for DLC coatings. The contents of Si in DLC films were changed by the flow rates of tetramethylsilane [TMS: $(CH_3)_4Si$] as 0, 0.5, 1.0, 2.0 and 3.5 sccm. The flow rate of toluene gas was set constant at 2.5 sccm, and the total gas pressure in the DLC coating process was set constant to 0.27 Pa.

Mirror polished stainless steel (SUS304) sheets (10×25×1 mm) were used as substrates. Si (100) wafer and glassy carbon sheets were also used as substrates for analyses of film thickness, internal stress and composition of films. DLC coating process consists of (1) Ar plasma sputter cleaning at −2 kV, (2) carbon ion implantation at −20 kV using CH_4 plasma, then (3) DLC deposition with −5 kV pulses under toluene and TMS plasma. Process times of (1), (2) and (3) were 30 min, 30 min and 2 h, respectively.

Silicon, carbon and hydrogen contents in the DLC films on glassy carbon substrates were measured by XPS (VG, Sigma Probe), and RBS and ERD using 2.8 MeV He^+ ion beam from a tandem type accelerator (NEC, 5SDH-2) with 70° incidence to the surface normal, respectively. Film thicknesses and internal stresses of DLC films were evaluated from step heights at the film edge and the curvature of DLC coated Si (100) substrates using a stylus profiler (Kosaka, ET-350), respectively. Hardness of the films was also measured with a dynamic-indentation tester (Akashi, MZT-5) with a Berkovich indenter at the maximum load of 2.5 mN.

Friction force or friction coefficient (FC) was measured by a reciprocating friction tester (Heidon, Type 22) with a steel (JIS-SUJ2 or AISI 52100) ball of 3-mm diameter. The length of sliding was 2 mm, the speed was 10 mm/s, and the load was 4.9 N. The load of 4.9 N, which is relatively high for usual friction tests by our tester, is applied to evaluate the adhesion strength of the films. The time of sliding was 40 min, or it is 3100 reciprocations. The tests were carried out at room temperature and at about 35% relative humidity. After the friction test, surfaces of DLC films and SUJ2 balls were observed using an optical microscope (Nikon, ME600) with Nomarski differential interference contrast. Section profiles of sliding traces were observed with a laser profiler (Keyence, VK-8510).

3. Results and discussion

Fig. 1 shows the surfaces of DLC films and SUJ2 balls after the friction tests. Thicknesses of DLC films were in the range of 410 to 740 nm, which were measured by a stylus profiler. Averaged values of friction coefficient (FC) in the last 5-min period of friction test are also shown in the figure. Without TMS flow (Fig. 1a), FC was the largest of 0.32, and the DLC film partly came off easily as seen as brighter contrast. A lot of debris and wear are observed on the counter ball. With the increase of TMS flow up to 1.0 sccm, the FC decreased to 0.14 and there was almost no peeling off of films, and the amount of debris and wear of the balls are relatively small. For the 2.0 sccm flow, the FC was 0.18 and there was a lot of debris on the DLC film and ball surfaces. For the 3.5 sccm flow, the FC decreased to 0.12 and the surface of DLC film is relatively smooth, although there were a lot of debris on both surfaces.

The width of sliding trace decreased with the TMS flow as shown in Fig. 1. Section profiles of the sliding traces are shown in Fig. 2. The depths of sliding traces are larger than the film thicknesses. It is very clear that the introduction of Si into DLC films by TMS flow can reduce wear of the films. In the cases of no TMS flow (0.0 sccm) and 2.0 sccm flow, there are clear peaks and valleys in the bottom regions. They represent the partial peeling off of DLC films as shown in Fig. 1.

The top profile in Fig. 2 represents the section profile of the DLC film after the indentation of 3-mm SUJ2 ball with 4.9 N for 30 min without stage movement of the friction tester for the 0.5 sccm flows of TMS. The dimple is not caused by a wear, but by a plastic deformation of the stainless steel substrate. This result suggests that the sliding traces are caused by not only the wear of films but also the plastic deformation of substrates. Thus, the wear of DLC film itself is relatively small compared to the cross-section of the trace, especially for the 0.5 and 1.0 sccm cases.

Hardness of DLC films evaluated from dynamic indentation tests and internal stress of the films obtained from the curvatures of Si wafer samples are shown in Fig. 3. It must be noted that the maximum penetration depths of the Berkovich indenter are about 80 to 90 nm, they are larger than the one-tenth of the film thicknesses (410–740 nm). Thus, the hardness we measured is affected by the softer substrate and became smaller than the intrinsic value of each DLC film.

The hardness gradually decreased with the increase of TMS flow up to 1.0 sccm, and it decreased drastically for 2.0 and 3.5 sccm. It can be said that too much Si doping is not good in order to maintain the high hardness of undoped DLC film. The apparent increase of debris on DLC film and ball for 2.0 and 3.5 sccm shown in Fig. 1 must be caused by this decrease of the hardness. The tendency of hardness decrease with the increase of Si content is the same as Si-DLC films prepared by PECVD [3,5].

On the other hand, the internal stress (compressive) of the films decreased with the increase of TMS flow. The difference of the internal stress between no TMS flow and 0.5 sccm flow is very drastic. Wu et al. [3] also showed the rapid decrease of internal stress at low Si content. Si doping in DLC films is a very useful technique for reducing internal stress of the film formed with PBII.